HIGH RESOLUTION MASS SPECTROMETRY FOR THE CHARACTERIZATION OF COMPLEX, FOSSIL ORGANIC MIXTURES

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INTRODUCTION

The nature of molecules with heteroatom functionality in the pyridine extracts of the Argonne Premium Coal Samples is being explored using high resolution mass spectrometry (HRMS), with desorption chemical ionization (DCI). Structural information is obtained from tandem MS experiments using high resolution to select the ions to fragment. The first DCIHRMS spectra of complex mixtures are shown. Molecular weight distribution determined by DCI are similar to those determined by laser desorption and field ionization mass spectrometry with very little ion intensity observed at greater than 1000 Daltons. Results are correlated with other techniques such as NMR, XPS, and XANES.

PyMS has been used extensively to examine coals and separated macerals. Results from electron impact (EI) in high resolution mode have demonstrated the importance of not only single heteroatom containing molecules in coals, but also multiple heteroatom containing molecules.[1] Both PyGCMS and PyMS have been used to analyze the more volatile pyrolysis components. Thermogravimetric MS techniques yield quantitative data with rather slow heating rates.[2] Also, a standard technique now used to provide molecular weight distribution of volatile tars is field ionization MS (FIMS).[3] FIMS results are published for all eight Argonne coals,[4] while Meuzelaar, Schulten and co-workers have correlated the results from PyFIMS, low voltage EI and TGAMS on the same coal.[5] They found similar patterns in the low mass regions. FABMS has been applied to coal pyrolysis products yielding data similar to FIMS.[6] Finally, the first DCIMS results have been discussed[7] and will be expanded in this paper with the addition of high resolution data.

EXPERIMENTAL

The Argonne Premium Coal samples used in this study have been described[8] and further information is available on World Wide Web - http://www.anl.gov/PCS/pcshome.html. Pyridine extracts[7] were thermalized directly in the source of a Kratos MS50 TA using a desorption chemical ionization probe heated from 200 to 700 °C @ 100 °C/min. The spectrometer was operated at a dynamic resolution of 10,000 and scanned at 10 s/decade of mass. Isobutane was used as the CI gas and poly(dimethylsiloxane) (PDMS) was used as the internal mass calibrant. For group analysis, all scans with ions above background are averaged and only those which occur a minimum of four times are saved. Formulae which fit within ±3.5 millimass units are assigned for each averaged ion peak. The formula are then sorted by hydrogen deficiency and heteroatom content.

RESULTS AND DISCUSSION

In general, the data from DCIHRMS are similar to those found by field ionization (FIMS).[4] A major problem is finding an internal mass calibrant because perfluorokerosene (pfk), which is used in electron impact, does not ionize in isobutane CI. PDMS is an effective calibrant,[9] but the measurements are not consistently as good as with pfk because the reference peaks are spaced at larger increments of mass. Therefore, we are looking at some alternative reference materials. Recently, a resolving power of 80,000 was achieved by the source used in this study.

Samples of averaged spectra are shown for four of the Argonne coals in Figure 1. The spectra typically show ion intensity out to $m/z \approx 700$ and useful information ends at the low mass end of 90, due to the isobutane. Normally [M+H]⁺ ions are observed under these conditions.

The subbituminous coal (Figure 1a) gave a distribution similar to bituminous coals, except for a series of fatty acids C_{25}, C_{27}, C_{29}, C_{31} (major) and C_{26}, C_{28}, C_{30} (minor). Also, pyrolysis fragments of lignin remnants are observed at $m/z = 111, 125, 139, 153$, which correspond to the series $Ph(OH)_2(CH_2)_xH$, $x = 0-3$. The acids were also observed in the lignite coal by DCIMS. With FIMS,

they were only observed in the lignite, but the lignin fragments are observed in both low rank coals.[4] It is interesting to note that these are not the major species seen by PyGCMS of low rank coals.

In the Illinois No. 6 coal (Figure 2b), the fatty acids are absent and the lignin derived pyrolysis fragments are alkylated C_0-C_4 monohydroxybenzenes. However, the molecular size distribution is very similar to the low rank subbituminous coal. Another difference is the large number of sulfur containing ions in the Illinois coal as one would expect.[1]

The hvA bituminous Pittsburgh seam coal gave a higher molecular size distribution of the ions. However, alkylated hydroxybenzene species are still observed, but their overall contribution to the total ion current found is significantly less than with the low rank coals.

The Blind Canyon coal (APCS 6) (Figure 1d) is unusual in that it contains significant amounts of resinite and sporinite macerals. Ions at m/z = 320 ($C_{25}H_{20}$), 321, 324 ($C_{25}H_{24}$), 325 (100), 342 ($C_{26}H_{30}$), 343 correspond to triterpenoid hydrocarbons from resinite, which has also been observed in Curie point pyrolysis MS[10] and by GCMS in benzene-methanol extract.[11]

All of the total ion response curves are bimodal such as is seen in Figure 2a for the Lewiston-Stockton hvA bituminous coal (APCS 7). This effect has also been seen in the temperature programmed thermolysis of whole coals. For the whole coal, the first peaks had been thought to be small molecules such as those that are solvent extractable. The extract also contains larger molecules which are released as pyrolysis temperatures where weak bond cleavage is occurring. No evidence is found for very large polycyclic aromatics volatilizing at the higher temperatures.

The change in the ion mass distribution with temperature for APCS 7 is shown in Figure 2b. The ions at m/z = 157 and 111 are artifacts from the extraction solvent, pyridine, representing the dimer of pyridine and an oxygenated alkyl pyridine molecule, respectively. At increasing desorption temperature, the size of the ions increases from scan 9 to scan 12. Around scan 18, pyrolysis begins and distribution shifts to small ions and finally the mass distribution shifts higher in scan 21. It is interesting to note that the distributions are similar in scan 12 and 21 even though the temperatures differ by 220 °C. In addition, over the entire temperature range, a series of distinct peaks are observed between 470 and 600. Exact mass measurements suggest that they are alkylated aromatic hydrocarbons with 4 rings. This was confirmed by tandem MS experiments and are possibly greatly modified biomarkers. They were not observed by FDMS, but have been seen in both FAB and EI MS experiments.[6,7]

Finally, from the exact mass measurement, formulae can be calculated resulting in information on ring size and heteroatom distribution. An example is shown in Figure 3 for the Pocahontas lv bituminous coal (APCS 5). The ring size varies from 4 to 7 with the most abundant being six (rings + double bonds = 18, 19). Even though the heteroatom content combined is lower than all the other coals, from statistical viewpoint every polycyclic aromatic with 6 rings should have a heteroatom in it. This is what we are observing in the extract. Some preliminary MSMS results suggest that annelated furans are the likely form of the single oxygen molecules, which agrees with NMR experiments.[12] XPS results indicate that over 60% of nitrogen exist in pyrrole type structures which is analogous to furan for oxygen and thiophene for sulfur.[13] These structures are probably important in determining the tertiary structure of high rank coals.

CONCLUSIONS

High resolution CIMS data further support the notion that the size of the stable aromatic clusters is not large in coals except the very high rank coals and inertinite macerals. The DCI spectra appear to be very representative of the sample with little discrimination for molecular types such as aliphatics.

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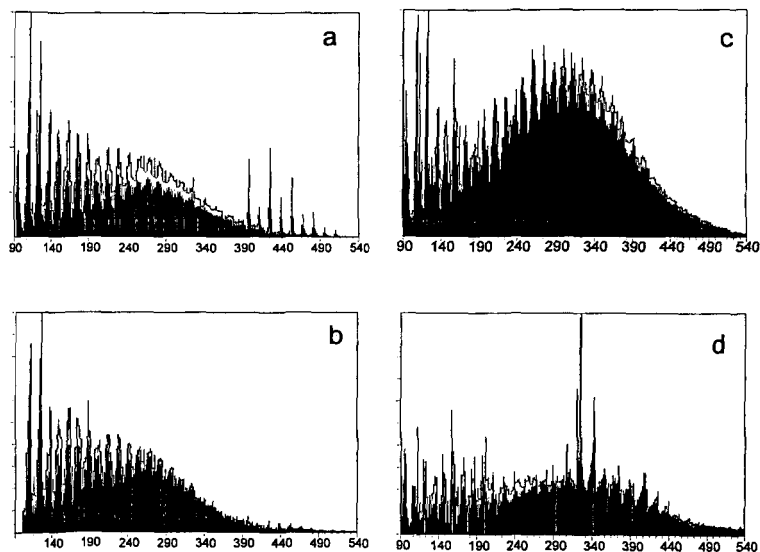
Figure 1. DCI mass spectra of selected Argonne coals. Data are derived from averaging over the total heating range. (a) Subbituminous coal (APCS 2); (b) Illinois No. 6 hvC (APCS 3); (c) Pittsburgh seam (APCS 4); and (d) Blind Canyon (APCS 6).
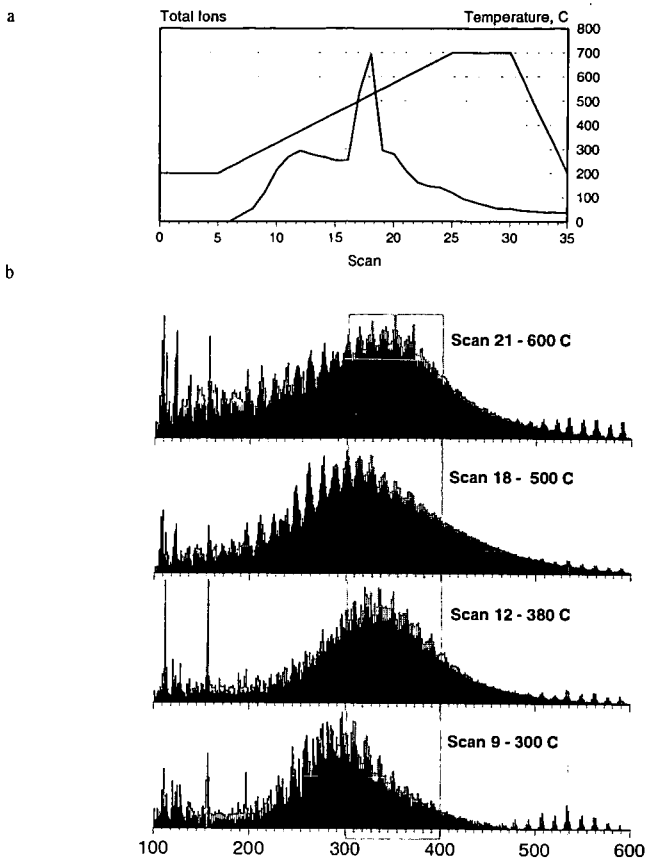
Figure 2. Data from Lewiston-Stockton bituminous coal(APCS 7). (a) Total ion response. (b) Selected scans labelled with scan numbers from Figure 2(a).
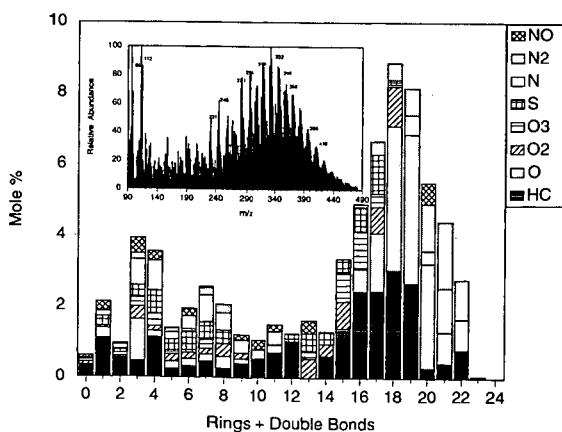

Figure 3. Group analysis of DCIHRMS data from Pocahontas extract(APCS 5). The inset is the averaged spectrum used to calculate the distributions.